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COMMUNICATION

Plutonium(IV) complexation by diglycolamide ligands—coordination chemistry insight into TODGA-based actinide separations†

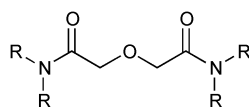
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Complexation of Pu(IV) with TMDGA, TEDGA, and TODGA diglycolamide ligands was followed by vis-NIR spectroscopy. A crystal structure determination reveals that TMDGA forms a 1 : 3 homoleptic Pu(IV) complex with the nitrate anions forced into the outer coordination sphere.

Processing used nuclear fuel and radioactive wastes allows recycling of the residual energy content and can significantly reduce the volume and radiotoxicity hazards associated with geological disposal of long-lived radioisotopes.¹ Removal or treatment of the actinides, and in particular transuranic isotopes, is central to achieving these goals. Accordingly, a wide range of actinide separations are under consideration for development. For example, diglycolamide (DGA) ligands, such as *N,N,N',N'*-tetraoctyl diglycolamide (TODGA), have shown great promise because of their affinity for trivalent actinides (An) and lanthanides (Ln).¹ Diglycolamide ligands also bind actinides in other oxidation states, such as Pu(IV). Indeed, TODGA has recently been studied as a ligand for group actinide extraction (GANEX) where all transuranics are extracted together.²

TODGA, R = n-C₈H₁₇

TMDGA, R = Me

TEDGA, R = Et

Surprisingly, very few coordination chemistry studies of DGAs with actinide ions have been conducted and the structure(s) of the An–DGA complexes formed and extracted

are still uncertain. There are no reported crystal structures containing the TODGA ligand, but there are a few Ln³⁺ and actinyl (UO₂²⁺, NpO₂²⁺) structures with DGA ligands where the octyl groups are replaced with shorter chain alkyl groups that facilitate crystallization of complexes.^{3–8} The Ln³⁺ : DGA structures are 1 : 3 complexes, while 1 : 1 and 1 : 2 structures have been reported for UO₂²⁺ and NpO₂²⁺. In solution, various studies have suggested that two, three, or four TODGA ligands can coordinate trivalent Ln³⁺/An³⁺ cations.¹ However, there are no structural reports of any plutonium complexes with DGA ligands. The need for Pu–DGA research was highlighted during solvent extraction tests of a TODGA-based system for a GANEX process, in which unexpected and deleterious precipitation of a Pu–TODGA-containing solid was observed, a phenomenon that does not occur for Th(IV), U(VI), or Ln(III). The exact composition of the solid is not known.²

In this communication, we report the complexation of TMDGA, TEDGA, and TODGA with Pu(IV). The first crystal structure of a Pu–DGA complex is presented, along with solid-state and solution characterization of the complex which suggests that the solid complex is stable when dissolved in solution.

TMDGA and TEDGA are water-soluble, and titration of these ligands into aqueous acidic solutions containing Pu(IV), analyzed by vis-NIR spectroscopy, provided initial evidence of Pu(IV)–DGA complexation (see ESI†). However, because our aim was to provide parallels to extractant chemistry we then looked for media in which both the short alkyl chain TMDGA/TEDGA and long alkyl chain TODGA ligands would be soluble. Published luminescence studies of Eu(III)–TODGA complexation in a mixed solvent EtOH : H₂O solution⁹ led us to focus on titrating TMDGA and TEDGA into EtOH solutions spiked with a Pu(IV)/HNO₃ acidic stock solution aliquot, with the anticipation that we could then compare to TODGA titrations in the same solution medium. The vis-NIR spectra reveal changes in the profile of the f–f and f–d electronic transitions as increasing equivalents of the ligand are added, consistent with complex formation (Fig. 1). Specifically, broad absorbances centered at 454, 642 and 1035 nm change in intensity while new absorptions at 763, 860 and 1080 nm appear and increase in intensity. However, even at a Pu : ligand ratio of 1 : 10 the bands at 860 and 1080 nm still appeared to be increasing in intensity without ‘full’ complexation

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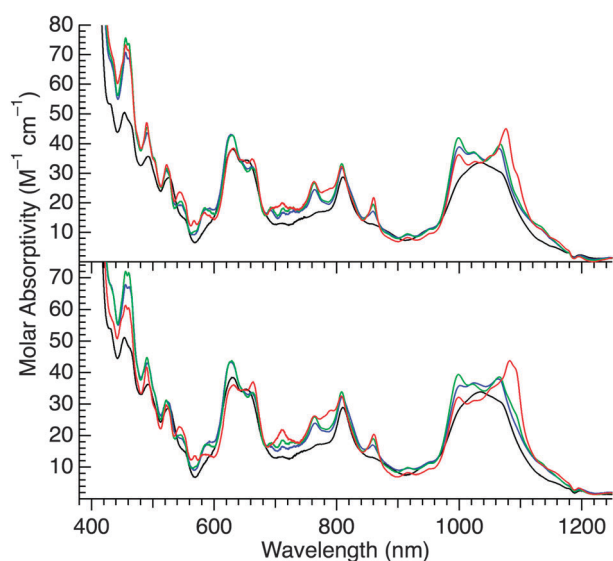


Fig. 1 Bottom: solution electronic absorption spectrum of 2.55–2.98 mM Pu(IV) in acidic EtOH as a function of added TMDGA. Top: spectrum of 2.53–2.98 mM Pu(IV) in acidic EtOH as a function of added TEDGA. Equivalents of added TMDGA or TEDGA: 0 (black), 1.5 (blue), 3.0 (green), 9.0 (red).

being reached. Excess HNO_3 from the Pu(IV) stock solution aliquot is likely preventing the limiting Pu–DGA complex species from being quantitatively formed (although evaporation of the 1 : 10 Pu(IV) : TMDGA solution from this titration in EtOH resulted in X-ray diffraction quality crystals of a 1 : 3 Pu : TMDGA complex—discussed later). Another complication is that the Pu starting material is likely a mixture of more than one species in aqueous–ethanol solutions with possible partial or complete displacement of inner sphere nitrate anions.¹⁰

The complications of excess HNO_3 and mixed H_2O –EtOH solvent media were subsequently avoided by preparing $[\text{TBA}]_2[\text{Pu}(\text{NO}_3)_6]$ (TBA = tetra-*n*-butylammonium) as a compositionally well-defined starting material,¹¹ and titrating this directly with TMDGA (and TEDGA) in MeCN solution (Fig. 2 and S6, ESI†). The vis-NIR spectra reveal changes in the profile of the f–f and f–d electronic transitions as increasing equivalents of the ligand are added, consistent with complex formation. Specifically, bands at 534, 607 and 744 nm diminish or change in intensity while new absorptions at 664 and 1087 nm appear and increase in intensity. The analogous titration with the longer octyl-chain bearing TODGA extractant was also performed, and the similarity in the spectra suggest that the solution complexes formed with Pu(IV) are similar for TMDGA, TEDGA and TODGA. Therefore, structural insights obtained on TMDGA or TEDGA complexes with Pu(IV) are likely to be good models for understanding the chemical interactions of TODGA (TODGA is unlikely to form complexes that can be crystallized).

Indeed, attempts to grow crystals of the Pu(IV)–TODGA complex yielded oils (due to the properties of the octyl chains) or decomposition products/starting material over long crystallization periods. For the shorter chain DGAs, we were able to grow orange crystals of $[\text{Pu}^{\text{IV}}(\text{TMDGA})_3](\text{NO}_3)_4 \cdot \text{MeCN}$ by treatment of $[\text{TBA}]_2[\text{Pu}(\text{NO}_3)_6]$ ¹¹ with 3 equiv. of TMDGA in MeCN, followed by solution evaporation or vapor diffusion

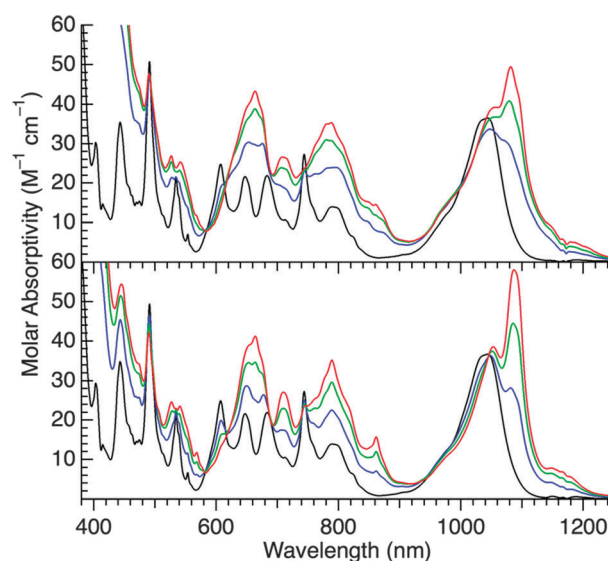


Fig. 2 Bottom: solution electronic absorption spectrum of 26.6–37.5 mM Pu(IV) in MeCN as a function of added TMDGA. Top: spectrum of 5.3–6.2 mM Pu(IV) in MeCN as a function of added TODGA. Equivalents of added TMDGA or TODGA: 0 (black), 1.0 (blue), 2.0 (green), 3.0 (red).

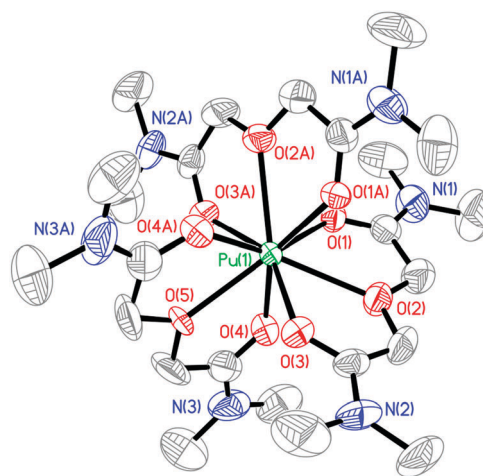


Fig. 3 Thermal ellipsoid plot (at the 50% probability level) of the solid-state structure of $[\text{Pu}^{\text{IV}}(\text{TMDGA})_3](\text{NO}_3)_4 \cdot \text{EtOH}$. Non-coordinating nitrate anions, lattice solvent and H atoms have been omitted for clarity. Pu(1) and O(5) sit on a two-fold symmetry axis and the 'A' atoms are generated by the symmetry operation $-x, y, \frac{1}{2} - z$.

with Et_2O . The same complex was also structurally determined, as $[\text{Pu}^{\text{IV}}(\text{TMDGA})_3](\text{NO}_3)_4 \cdot \text{EtOH}$ (Fig. 3), from orange crystals obtained by evaporation of the 1 : 10 Pu(IV) : TMDGA titration in EtOH– HNO_3 described earlier. Although this method was not a rational stoichiometric synthesis like the MeCN route, we will use the EtOH solvate structure for the purposes of discussion of the metrical details because of the higher quality X-ray diffraction data (Table S1, ESI†). The Pu(IV) ion has a coordination number of nine and is bonded to three tridentate TMDGA ligands, each of which is bound to the metal through two C=O donor groups and one ether C–O–C group. The coordination geometry is best described as twisted tricapped trigonal prismatic, in which the three C–O–C ether O atoms occupy the capping positions and

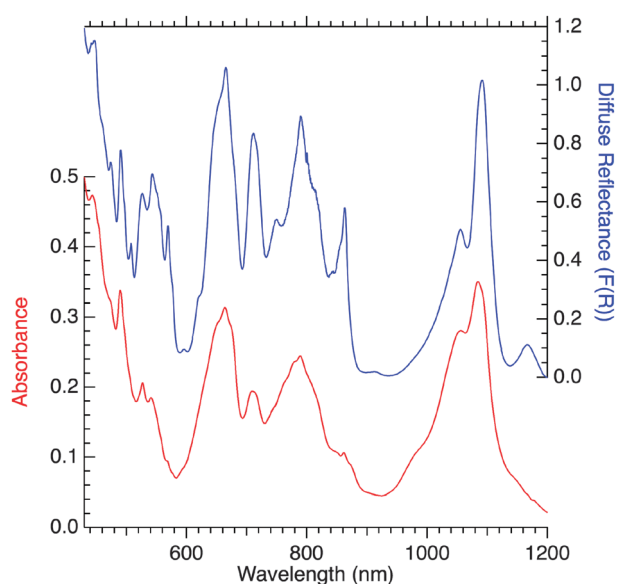


Fig. 4 Vis-NIR diffuse reflectance spectrum of solid $[\text{Pu}^{\text{IV}}(\text{TMDGA})_3](\text{NO}_3)_4 \cdot \text{MeCN}$ (blue spectrum, right axis). The solution electronic absorption spectrum of the above crystals dissolved in MeCN (red spectrum, left axis) is shown for comparison.

the two trigonal faces are formed by the C=O atom groups O1, O3A, O4, and O1A, O3, O4A (with a 'twist angle' between the two faces of 16.1°). The three independent Pu–O_(C=O) distances are 2.317(6), 2.297(6), and 2.284(7) Å, whilst the two independent Pu–O_(C–O–C) distances are substantially longer at 2.504(6) and 2.437(8) Å.

The homoleptic 1 : 3 Pu : TMDGA complex type is similar to known DGA complexes with Ln(III) ions.^{1,4,5,7} For example, $[\text{La}\{\text{T}(\text{iBu})\text{DGA}\}_3][\text{La}(\text{NO}_3)_6]$ contains tridentate DGA ligands with the Ln–O_(C=O) bonds *ca.* 0.2 Å longer than the Pu–O_(C=O) bonds,⁷ which is likely a reflection of the reduced electrostatic interactions for Ln^{3+} vs. Pu^{4+} towards the DGA ligands. Similarly, the Ln–O_(C–O–C) bond is *ca.* 0.08 and 0.14 Å longer than the two independent Pu–O_(C–O–C) bonds in $[\text{Pu}^{\text{IV}}(\text{TMDGA})_3](\text{NO}_3)_4 \cdot \text{EtOH}$. A 1 : 3 T(iPr)DGA complex with the much smaller Yb^{3+} ion (compared to La^{3+}) exhibits shorter Yb–O bond lengths closer to those in the Pu(IV)–TMDGA complex.⁴ There are no reported molecular structures of DGA ligands with An(IV) ions for direct comparison to Pu(IV). Both 1 : 1 and 1 : 2 DGA complexes with the $\text{U}^{\text{VI}}\text{O}_2^{2+}$ cation have been structurally determined,^{7,8} as has a 1 : 2 complex of TMDGA with the $\text{Np}^{\text{V}}\text{O}_2^+$ cation.⁶ In all these cases, the DGA ligands bind in a tridentate 'O₃' mode.

The $[\text{Pu}^{\text{IV}}(\text{TMDGA})_3](\text{NO}_3)_4 \cdot \text{MeCN}$ crystals, obtained in 47% yield, were ground into a powder and the diffuse reflectance vis-NIR spectrum was collected (Fig. 4, blue). Some of these crystals were dissolved in MeCN to compare the solution vis-NIR spectrum to the solid diffuse reflectance spectrum (Fig. 2, red). The similarity in the solution and solid state spectra suggests that the $[\text{Pu}(\text{TMDGA})_3]^{4+}$ species persists in solution. Some crystals were also dissolved in MeCN-*d*₃ and the ¹H NMR spectrum was recorded, revealing two paramagnetically broadened resonances at 2.6 and 3.6 ppm (two resonances are expected, arising from the N(CH₃)₂ protons and the C–CH₂–O–CH₂–C protons of the ligand).

In the TODGA-based Pu(IV) extraction study reported by Brown *et al.*, the tan/brown precipitate that unexpectedly formed at the interface between the organic and aqueous solution phases was compositionally undetermined, but gamma spectroscopy indicated that it contained Pu while infrared spectra showed evidence for complexed TODGA and coordinated nitrate.² We therefore obtained a nujol mull FT-IR spectrum of solid $[\text{Pu}^{\text{IV}}(\text{TMDGA})_3](\text{NO}_3)_4 \cdot \text{MeCN}$ for comparison (see ESI†). As expected from the crystal structure, the IR spectrum does not indicate coordinated nitrate. Possible explanations for why Brown *et al.* observed both bound TODGA and coordinated nitrate are that multiple Pu products precipitated (*e.g.* $[\text{Pu}(\text{TODGA})_3](\text{NO}_3)_4$ and other species with bound inner sphere nitrate), or there is coordinated nitrate in a Pu–TODGA complex, perhaps suggesting fewer than three TODGA ligands are bound to Pu(IV) due to nitrate competition from the high NO_3^- concentration in the acidic phase and/or formation of complex Pu–TODGA– NO_3^- (inner sphere) aggregates upon extraction.

In conclusion, the crystal structure of a Pu–DGA complex has been reported revealing a 1 : 3 Pu : DGA stoichiometry. The similarity of solid state and solution vis-NIR spectra suggest that this 1 : 3 complex also exists in solution. These results provide data on the basic bonding properties of DGA ligands to Pu(IV), which was previously unknown. The similarity between TODGA and TMDGA/TEDGA solution spectra suggest that TODGA is also forming a 1 : 3 complex with Pu(IV) under the same conditions, thus demonstrating the utility of short chain DGA ligands as models for the chemistry of the 'oily' longer chain kerosene-soluble TODGA separation agent. Further studies are required to introduce the chemical complexity of biphasic extraction conditions into the system (excess nitrate, presence of acid, synergist, *etc.*) in order to elucidate the precise species and complexes that form during separation processes.

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